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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) **Brightener-Containing Paper-Coating Compositions**

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S1601-23

Notice: The specification contained herein as filed

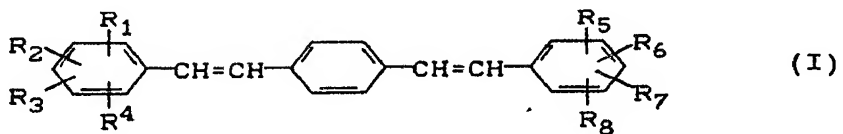
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CCA 3254 (10-89) 41

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Abstract

Paper-coating compositions containing compounds of the formula



wherein R_1 , R_2 , R_3 and R_5 , R_6 , R_7 denote H, F, Cl or CH_3 and R_4 and R_8 denote H, $\text{O-C}_1\text{-C}_4\text{-alkyl}$, $\text{S-C}_1\text{-C}_4\text{-alkyl}$, $\text{SO}_2\text{C}_1\text{-C}_4\text{-alkyl}$, CF_3 , OCF_3 or SCF_3 , are inexpensive and are distinguished by high brightness.

For optical brightening of coating compositions based on plastics dispersions, substantive anionic brighteners are normally employed. However, in the coating compositions, these brighteners show only very unsatisfactory brightening effects, a very low greying limit and too little light-fastness.

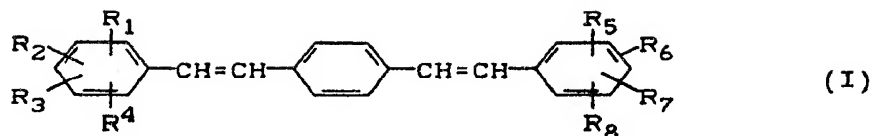
It is generally known partially to solve the said difficulties by adding hydrophillic co-binders or carriers to the coating composition. (Compare "Das Papier" 36 (1982), 66, DE-A-3,502,038 and EP-A-43,790).

Although the brightening effect can be significantly improved in this way, the water sensitivity of the coated papers is increased at the same time.

It is also known (compare DE-A 3,112,435) to cause water-soluble brighteners to be absorbed on certain plastics such as, for example, urea resins or methylol resins, and to add these brightened plastics as a dispersion to the paper coating composition.

Finally, it has been proposed (DE-A 3,643,215) to employ water-insoluble salts of anionic brighteners and long-chain fatty amines for paper coating. However, these proposals have so far been unable to gain acceptance because of their excessive costs or because of rheological difficulties.

It has now been found, surprisingly, that coating compositions for paper coating can be brightened without the said disadvantages, if brighteners of the formula



wherein - independently of one another - R_1 , R_2 , R_3 and R_5 , R_6 , R_7 denote H, F, Cl or CH_3 and R_4 and R_8 denote H, O- C_1 - C_4 -alkyl, S- C_1 - C_4 -alkyl, SO_2C_1 - C_4 -alkyl, CF_3 , OCF_3 or SCF_3 ,
 5 it also being possible for two adjacent radicals to represent $-\text{OCH}_2\text{O}-$ or $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$,
 are added to the coating compositions.

Preferably, the alkyl radicals represent methyl radicals.

10 The invention also relates to novel compounds of the formula I, wherein

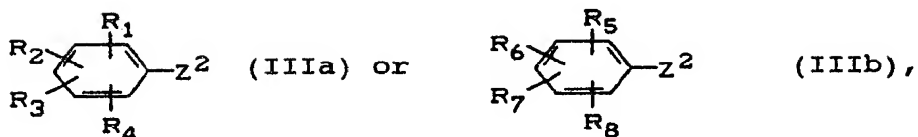
R_4 and R_8 F, CF_3 , OCF_3 or SCF_3

and the remaining radicals have the meaning given above, with the proviso that these
 15 radicals do not represent hydrogen if R_4/R_8 denote F or CF_3 .

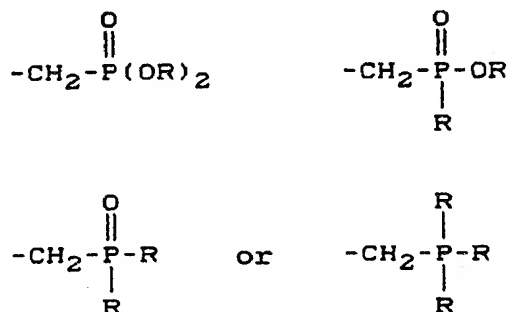
The distyryl compounds of the formula (I) can be prepared according to methods known per se by reacting a compound of the formula



in the desired ratio with in each case one compound of the formulae



one of the symbols Z_1 and Z_2 in each case representing a formyl group and the other representing a grouping of the formula



wherein

R denotes a $\text{C}_1\text{-C}_4$ -alkyl, $\text{C}_5\text{-C}_6$ -cycloalkyl or an optionally further substituted aryl radical, preferably a phenyl radical.

In this way, symmetrical and unsymmetrical compounds and mixtures of symmetrical and unsymmetrical compounds can be prepared.

The phosphorus compounds of the formulae (IIIa), (IIIb) and (II) required here as starting materials are obtained by reacting halogenomethyl compounds, preferably chloroethyl or bromomethyl compounds of the formulae



and



with phosphorus compounds P(OR)_3 , R-P(OR)_2 , RO-P(R)_2 or P(R)_3 , R having the meaning indicated. Preferably, R denotes $\text{C}_1\text{--C}_4\text{-alkyl}$ if bound to oxygen, but phenyl if bound to phosphorus.

To prepare the final substances, the corresponding components are condensed in organic solvents in the presence of basic condensing agents.

The solvents selected are advantageously inert solvents, for example hydrocarbons such as toluene or xylene, or alcohols such as methanol, ethanol, isopropanol, butanol, glycol, glycol ethers such as 2-methoxyethanol, hexanol, cyclohexanol or cyclooctanol, and also ethers such as diisopropyl ether, dioxane or tetrahydrofuran; moreover formamides, N-methylpyrrolidone, dimethyl sulphoxide and phosphoric acid amide. Dimethylformamide, dimethylacetamide and phosphoric acid tris-dialkylamides, alkyl being in particular $\text{C}_1\text{--C}_4\text{-alkyl}$, are preferred.

The condensing agents used can be strongly basic compounds such as alkali metal hydroxides or alkaline earth metal hydroxides, alkali metal amides or alkaline earth metal amides and alkali metal alcoholates or

alkaline earth metal alcoholates, for example potassium hydroxide, sodium hydroxide, potassium tert.-butylate, sodium amide or sodium methylate, and also the alkali metal compounds of dimethyl sulphoxide and alkali metal hydrides as well as, if appropriate, alkali metal dispersions.

The reactions are preferably carried out in the temperature range from 0 to 120°C.

The compounds (I) according to the invention are also obtained when the corresponding aldehyde anils are reacted in a dipolar aprotic solvent such as dimethylformamide in the presence of basic condensing agents with the corresponding methyl compounds.

In the dissolved or finely dispersed state, the compounds of the formula (I) show a very strong blue fluorescence. They are suitable, individually or as a mixture, for brightening the most diverse synthetic, semi-synthetic or natural organic materials.

Particularly preferred fields of application of the compounds and mixtures of the formula (I) is the use in paper-coating compositions.

The brighteners can be used as brightening agents directly or after preceding fine grinding or liquid formulating.

The liquid formulations can be prepared as follows:

The press cakes and/or powders are, after addition of a surface-active material and/or dispersant and optionally water, homogenized with vigorous stirring. Subsequently, the quantity of these auxiliaries can be

increased optionally to the total quantity required for the stability of the dispersion.

The suspension obtained is then pre-comminuted and wet-ground.

5 The pre-comminution can be carried out by means of stone mills or toothed colloid mills.

10 The subsequent wet comminution can be carried out in colloid mills, oscillating mills, cone mills and vibro mills and also in dissolvers or in ball mills, or in sub-micron dispersers. Preferably, however, continuously running stirred mills with grinding bodies, preferably those of SiO_2 of 0.1 to 5 mm, in particular 0.2-2 mm diameter, are used. The grinding step is complete when a particle size of the product of $< 5 \mu\text{m}$, preferably

15 $< 0.5 \mu\text{m}$ has been reached.

20 After the grinding treatment, further quantities of surface-active materials or also hydrotropic substances such as, for example, ethylene glycol or glycerol, preservatives, wetting agents, antifoams, dedusting agents and/or water can optionally also be added, unless this has already been done at an earlier point in time, for example before grinding.

25 The dispersions prepared by this process contain 5 to 50 %, preferably 10 to 30 % of the brightener salts according to the invention, which are sparingly soluble or insoluble in water, 1 to 50 %, preferably 5 to 20 % of surface-active materials or dispersants, 0 to 5 % of preservatives and water, it being possible for a part of the water to be replaced by hydrotropic substances (% =

30 per cent by weight).

The surface-active materials used can be any conventional, cationic and nonionic surface-active materials such as are described, for example, in DE-OS (German Published Specification) 2,334,769, pages 8 to 10 (corresponds to British Patent Specification 1,417,071).

Preferably, nonionic surfactants are used. Suitable anionic dispersants are conventional formaldehyde condensation products of arylsulphonamines, sulphonated diaryl ethers and diaryl sulphones and others.

The paper-coating compositions, in which the brighteners to be used according to the invention are incorporated, have the following structure: plastic dispersions based on styrene/butadiene copolymers, carboxylated styrene/butadiene copolymers or polyvinyl acetate copolymers or of acrylic acid esters in combination with white pigments, both without and with small quantities of hydrophilic co-binders.

The quantity of the compounds I employed depends on the desired brightening effect. In general, 0.01 to 0.5 % by weight of pure active substance (relative to the solids content of the paper-coating composition to be brightened) is sufficient. One particular advantage is that, depending on the composition of the coating compositions, the attainable greying limit (up to which a further addition of brightener still produces additional effects) is extremely high.

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Example 1



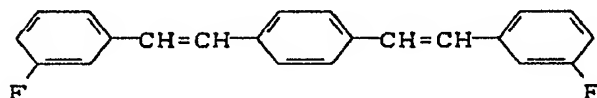
- 5 a) 40 g (0.1 mol) of p-xylylene diethyl bisphosphonate (93.4 % pure) are initially introduced together with 23.3 g (0.22 mol) of benzaldehyde into 100 ml of dimethylformamide. To this, 39.6 g (0.22 mol) of a 30 % strength sodium methylate solution are added dropwise at room temperature under nitrogen. The mixture is stirred for 2 hours at room temperature and for a further 30 minutes at 60°C. After cooling, 10 the mixture is filtered with suction. This gives 19.8 g (70.2 %) of distyrylbenzene in the form of slightly yellow crystals which, after reprecipitation from toluene/Tonsil, melt at 173°C. Extinction in DMF: $\lambda_{\text{max}} = 355.9 \text{ nm}$; $\epsilon = 6600$.
- 15 b) 250 g of the crystalline brightener are mixed with 200 g of benzylphenylphenol with 14 ethylene oxide and 550 g of water and subjected to a pre-comminution on a corundum disc mill and ground until an average particle size of less than 50 μm is obtained. 20 Grinding is then continued with glass beads of 0.2 mm diameter in a stirred mill down to an average particle size of less than 0.5 μm . The fine dispersion obtained can immediately be incorporated into the paper-coating composition ready for 25 application.

- c) 150 g of a formaldehyde condensation product of the Na salt of ditolyl ether-sulphonic acid and 550 g of water are added to 300 g of the crystalline brightener, and the mixture is treated as in Example 1b.
- 5 After fine grinding, a further 200 g of the condensation product of formaldehyde and the Na salt of ditolyl ether-sulphonic acid and 200 g of the condensation product of formaldehyde and the Na salt of naphthalenesulphonic acid as well as 50 g of a
- 10 mineral oil emulsion (10 % aqueous) are added.

The suspension is then subjected to a spray-drying process and, at about 5 % residual moisture content, dried to give granules containing 30 % of active substance, which can then be incorporated under a

15 high-speed stirrer into the paper-coating composition ready for application.

Example 2



24.6 g (0.1 mol) in fluorobenzyl ether phosphonate and 6.5 g (0.05 mol) of terephthalaldehyde are

20 initially introduced under nitrogen into 50 ml of dimethylformamide. At room temperature, 18 g (0.1 mol) of 30 % strength sodium methylate solution are added dropwise, and the mixture is stirred for 2 hours at room

temperature and for one further hour at 60°C. After cooling, the mixture is filtered with suction, and 24.5 g (77 %) of bis-(m-fluorostyryl-)benzene are obtained as colourless crystals which, after reprecipitation from toluene/Tonsil, melt at 188-190°C. Extinction in DMF: $\lambda_{\max} = 355.9 \text{ nm}$; $\epsilon = 61,200$.

Examples 3 - 48

Analogously to the procedures of Examples 1 and 2, the brighteners listed in the table which follows are obtained:

Table

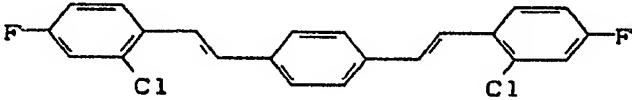
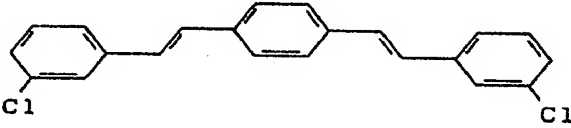
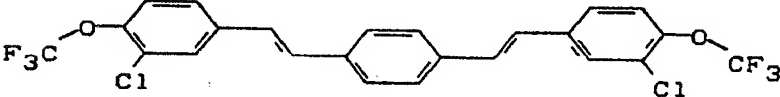
Ex-ample	Formula	Extinction in DMF
3		$\lambda = 359.9 \text{ nm}$ $\epsilon = 48,500$
4		$\lambda = 358.4 \text{ nm}$ $\epsilon = 66,500$
5		$\lambda = 359 \text{ nm}$ $\epsilon = 67,000$

Table (continuation)

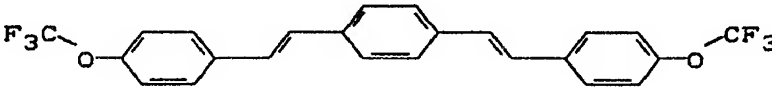
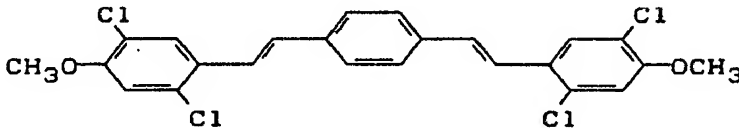
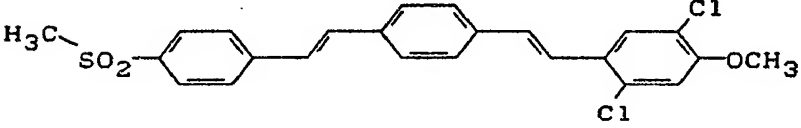
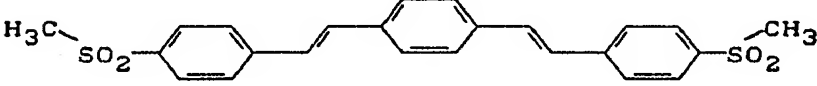
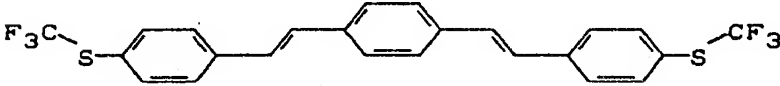
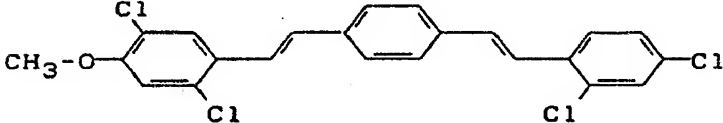
Ex-ample	Formula	Extinction in DMF
5	6	
		$\lambda = 357.1 \text{ nm}$ $\epsilon = 66,000$
10	7	
		$\lambda = 371 \text{ nm}$ $\epsilon = 67,700$
	8	
		$\lambda = 370.4 \text{ nm}$ $\epsilon = 68,200$
15	9	
		$\lambda = 369.7 \text{ nm}$ $\epsilon = 80,800$
	10	
		$\lambda = 368.5 \text{ nm}$ $\epsilon = 74,600$
20	11	
		$\lambda = 371 \text{ nm}$ $\epsilon = 61,800$

Table (continuation)

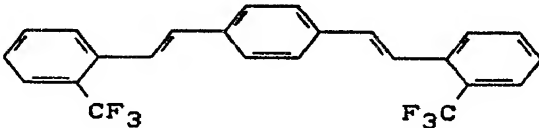
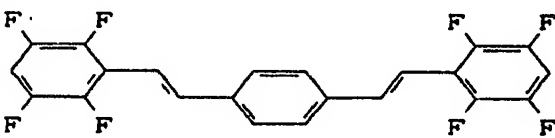
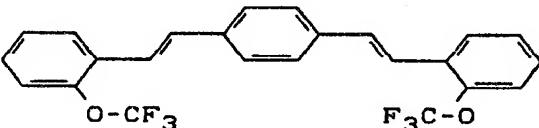
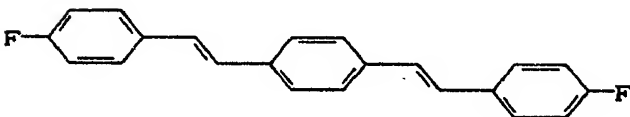
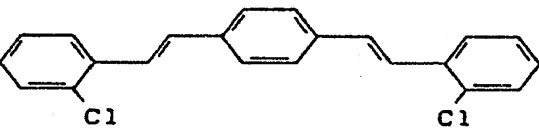
Ex-ample	Formula	Extinction in DMF
5	12	
		$\lambda = 348.6 \text{ nm}$ $\epsilon = 56,000$
10	13	
		$\lambda = 351.7 \text{ nm}$ $\epsilon = 55,800$
	14	
		$\lambda = 354.6 \text{ nm}$ $\epsilon = 57,000$
15	15	
		$\lambda = 354.5 \text{ nm}$ $\epsilon = 62,000$
	16	
		$\lambda = 355.9 \text{ nm}$ $\epsilon = 55,000$

Table (continuation)

Ex- ample	Formula	Extinction in DMF
5	17	
		$\lambda = 355.9 \text{ nm}$ $\epsilon = 63,500$
	18	
10		$\lambda = 367.6 \text{ nm}$ $\epsilon = 69,000$
	19	
		$\lambda = 367 \text{ nm}$ $\epsilon = 66,800$
	20	
15		$\lambda = 367 \text{ nm}$ $\epsilon = 66,800$
	21	
		$\lambda = 363.6 \text{ nm}$ $\epsilon = 73,700$

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Table (continuation)

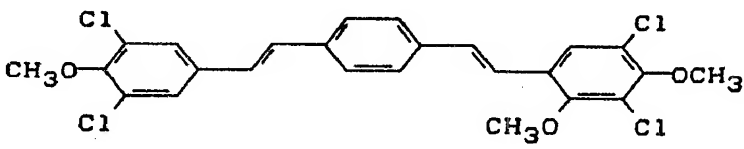
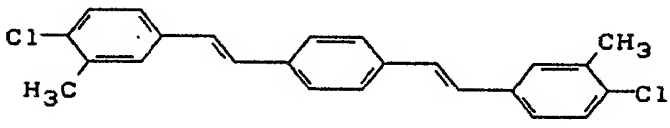
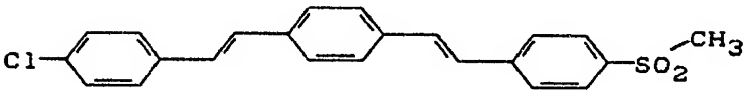
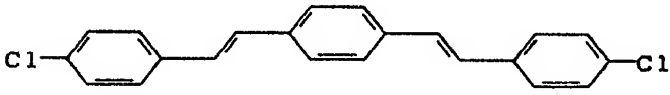
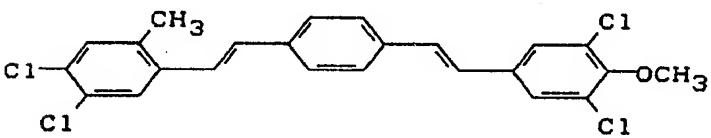
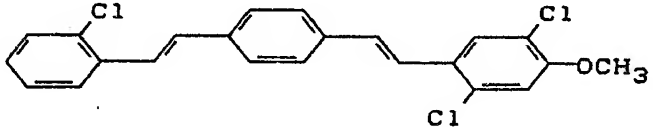
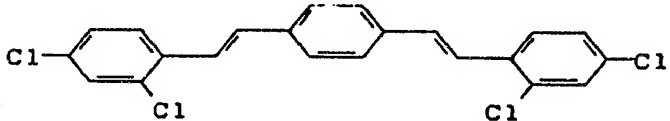
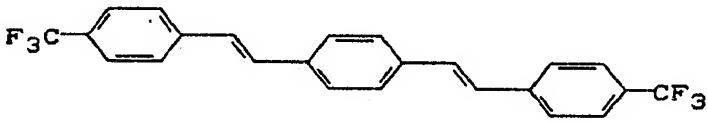
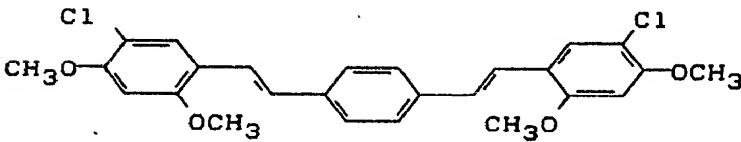
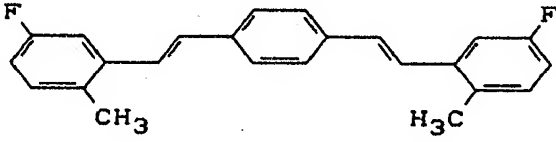
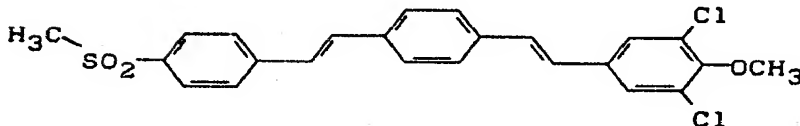
Ex- ample	Formula	Extinction in DMF
5	22	 $\lambda = 365 \text{ nm}$ $\epsilon = 69,600$
10	23	 $\lambda = 363 \text{ nm}$ $\epsilon = 73,000$
	24	 $\lambda = 362.9 \text{ nm}$ $\epsilon = 83,700$
15	25	 $\lambda = 362.3 \text{ nm}$ $\epsilon = 71,500$
	26	 $\lambda = 361.7 \text{ nm}$ $\epsilon = 55,000$
20	27	 $\lambda = 361.7 \text{ nm}$ $\epsilon = 60,000$

Table (continuation)

Ex-ample	Formula	Extinction in DMF
5	28	
		$\lambda = 361.7 \text{ nm}$ $\epsilon = 60,000$
	29	
10		$\lambda = 361 \text{ nm}$ $\epsilon = 69,600$
	30	
		$\lambda = 582.4 \text{ nm}$ $\epsilon = 61,500$
	31	
15		$\lambda = 358.4 \text{ nm}$ $\epsilon = 61,000$
	32	
		$\lambda = 367 \text{ nm}$ $\epsilon = 80,000$

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Table (continuation)

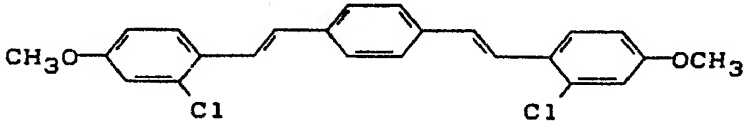
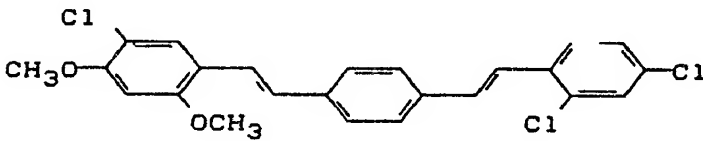
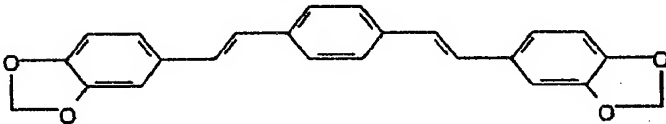
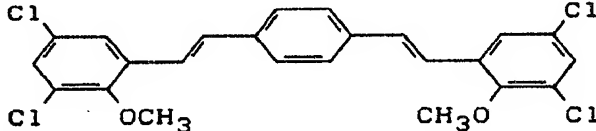
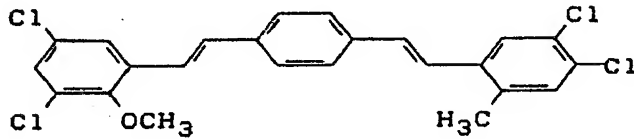
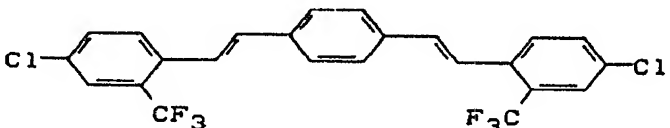
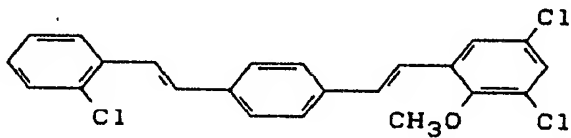
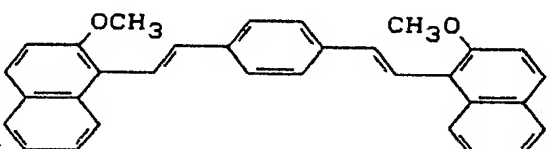
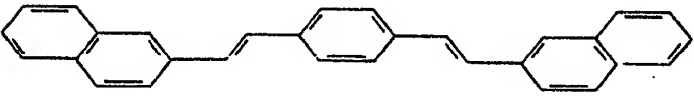
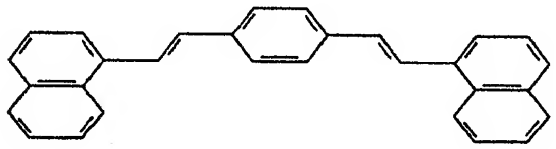
Ex- ample	Formula	Extinction in DMF
5	33	
		$\lambda = 367.6 \text{ nm}$ $\epsilon = 71,000$
10	34	
		$\lambda = 366.3 \text{ nm}$ $\epsilon = 58,500$
	35	
		$\lambda = 373.4 \text{ nm}$ $\epsilon = 68,500$
15	36	
		$\lambda = 366.3 \text{ nm}$ $\epsilon = 54,500$
	37	
		$\lambda = 365.3 \text{ nm}$ $\epsilon = 58,000$

Table (continuation)

Ex- ample	Formula	Extinction in DMF
5	38	
		$\lambda = 363.11 \text{ nm}$ $\epsilon = 71,000$
10	39	
		$\lambda = 355.9 \text{ nm}$ $\epsilon = 61,200$
	40	
		$\lambda = 364.3 \text{ nm}$ $\epsilon = 62,500$
15	41	
		$\lambda = 363.1 \text{ nm}$ $\epsilon = 67,500$
	42	
		$\lambda = 370.4 \text{ nm}$ $\epsilon = 58,000$
20	43	
		$\lambda = 368.3 \text{ nm}$ $\epsilon = 60,000$

Table (continuation)

Ex-ample	Formula	Extinction in DMF
5	44	
		$\lambda = 347.8 \text{ nm}$ $\epsilon = 52,000$
	45	
10		$\lambda = 358.4 \text{ nm}$ $\epsilon = 62,500$
	46	
		$\lambda = 381.7 \text{ nm}$ $\epsilon = 42,000$
	47	
15		$\lambda = 375.2 \text{ nm}$ $\epsilon = 66,000$
	48	
		$\lambda = 373.8 \text{ nm}$ $\epsilon = 52,000$

Example 49

A paper-coating composition having a solids content of about 55 % is prepared by stirring together 60 parts of SPS china clay

5 40 parts of calcium carbonate

20 parts of an anionic plastics dispersion of an acylic acid ester-containing copolymer having a solids content of about 50 % (for example Acronal S 320 D[®] from BASF)

10 5 parts of a polyacrylic acid ester as a co-binder (40 % strength) (for example Acrosol 40 D[®] from BASF) and

80 parts of water,

and the pH value of the composition is adjusted to 9 with sodium hydroxide solution.

15 10 g, 20 g, 40 g, 60 g or 100 g of a 25 % strength dispersion of the optical paper brightener of Example 1b) are stirred in each case into one 1 kg of this coating composition.

20 After the prepared coating composition has been coated onto paper with the aid of a manual coating blade or an experimental coating unit and after drying at 80°C, coated papers are obtained which, depending on the addition of brightener, show a significant to excellent
25 brightening effect. In contrast to conventional paper brighteners, a significant increase in whiteness is still achievable without a co-binder, even at higher brightener additions such as, for example, 50 g/kg of coating compound.

30 Table 1 shows the CIE whiteness of the coated papers.

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Table 1

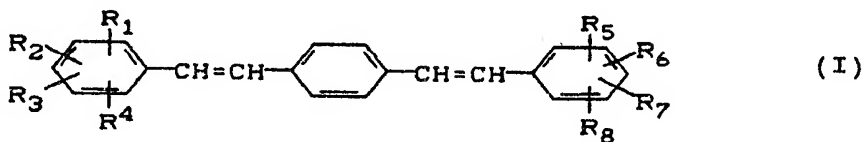
25 % strength brightener dispersion
(Example 1b)
(g/kg of coating compound)

CIE
whiteness

5	-	63.0
	10	88.0
	20	99.0
	40	113.2
	60	121.2
10	100	128.3

Patent Claims

1. Brightener-containing paper-coating compositions containing, as the brightener, compounds of the formula



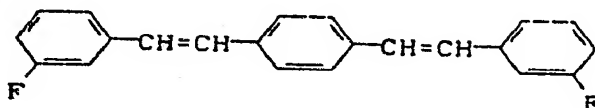
wherein - independently of one another - R_1 , R_2 , R_3 and R_5 , R_6 , R_7 denote H, F, Cl or CH_3 and R_4 and R_8 denote H, O- C_1 - C_4 -alkyl, S- C_1 - C_4 -alkyl, SO_2C_1 - C_4 -alkyl, CF_3 , OCF_3 or SCF_3 ,

it also being possible for two adjacent radicals to represent $-OCH_2O-$ or $-CH=CH-CH=CH-$.

2. Paper-coating compositions according to Claim 1, characterized in that they contain the compound of the formula

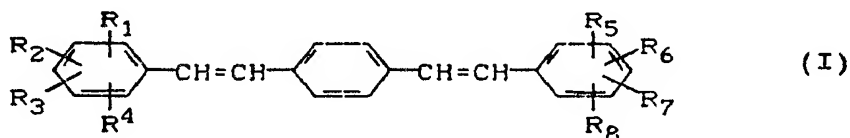


3. Paper-coating compositions according to Claim 1, characterized in that they contain the compound of the formula



4. Paper-coating compositions according to Claim 1, characterized in that the average particle size of the brighteners is less than 5 μm , preferably less than 0.5 μm .

5. Compounds of the formula

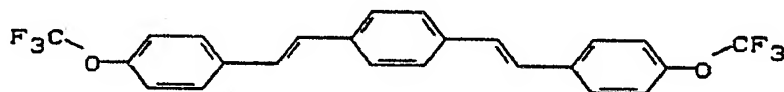


wherein

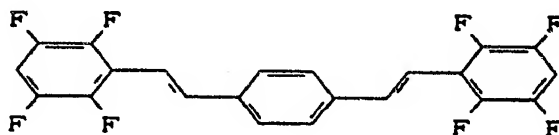
R_4 and R_8 F, CF_3 , OCF_3 or SCF_3

and the remaining radicals have the meaning given above, with the proviso that these radicals do not represent hydrogen if R_4/R_8 denote F or CF_3 .

6. Compound of the formula



7. Compound of the formula



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SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente